Rapid charging made practical in graphite-based lithium batteries: surface acoustic wave turbulent electrolyte mixing to overcome diffusion limited charging rates

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2020 DOE Vehicle Technologies Office Annual Merit Review

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Project ID # bat392

Overview

Timeline of the project
- Start: June 2018
- End: June 2020
- 80% complete

Budget
- Total project funding from DOE: $680,000

- Funding for FY2019: $283,000
- Funding for FY2020: $397,000

Barriers and Technical Targets
- Technical targets: increase the energy density to 180Wh/kg at 10 mins charge time, retaining 80% energy density after 500 cycles in a 2Ah pouch cell format.

- Barriers: Showed significantly improved performance with SAW when integrated in the cell, but still not achieving energy density goal, battery chemistry & construction requires improvement.

Partners
- Interactions / collaborations:
  - UCSD Qualcomm Institute
  - Oak Ridge National Laboratory
  - LiFung battery manufacturer
- Project lead: UC San Diego

Relevance

- **Impact**
  - Substantially improved Li ion diffusion rates in lithium batteries from acoustic streaming generated by an integrated acoustic device
  - Significantly improved both power density and energy density of lithium batteries

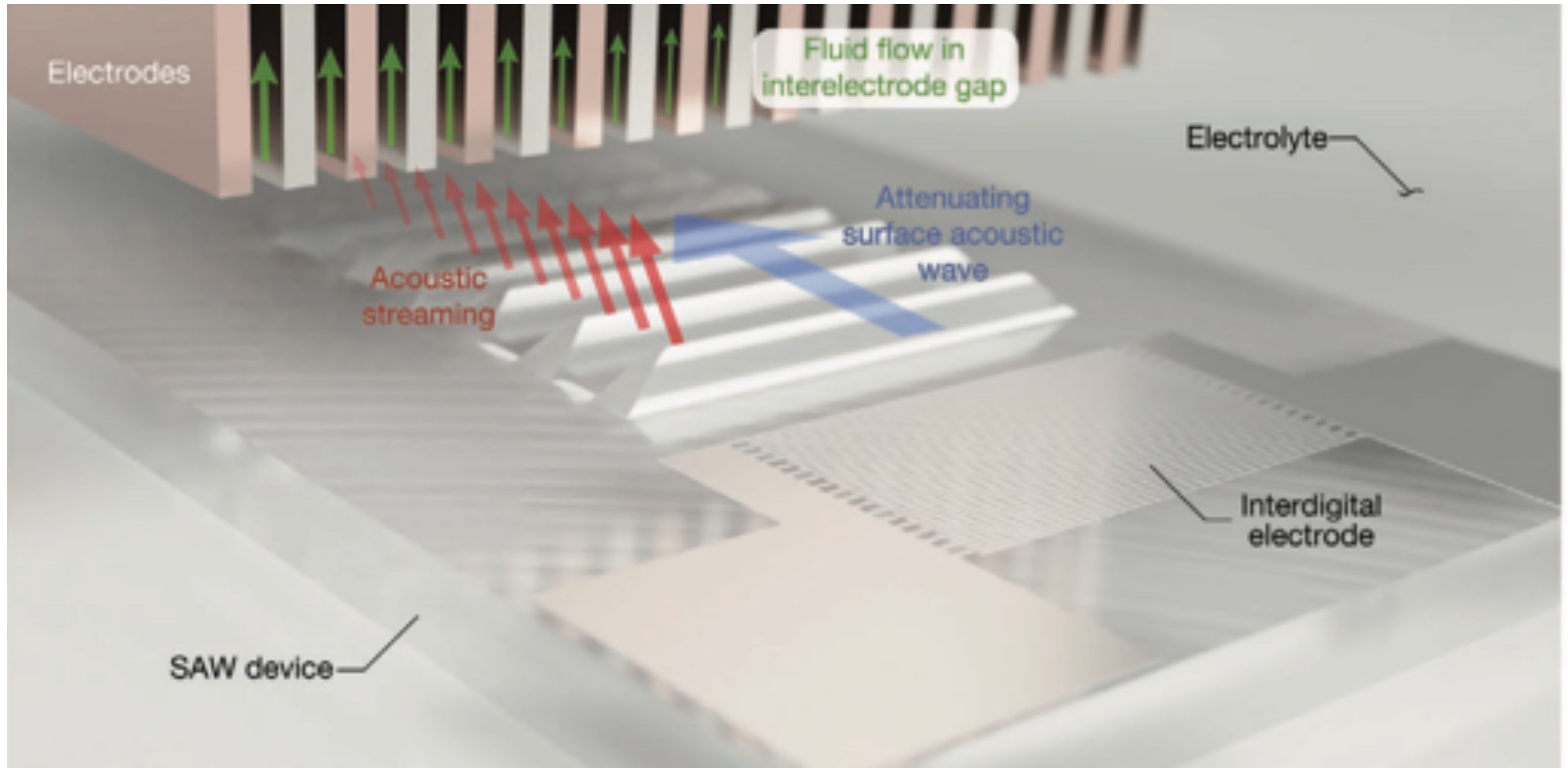


Illustration of the interaction of SAW with an LIB

- **Objective**
  - Develop integration scheme for surface acoustic wave devices to enhance inter-electrode diffusivity
  - Understand the electrode interfacial material degradation behavior with and without SAW
  - Devise closed-form math model to represent Li diffusion in presence of acoustically driven flow, correlate with transparent battery analog in experiment

Milestones

Quarter	Milestones	Status
Sep 2019	Portable circuit design complete, including automatic sequencing of signal generator and battery cycler.	Completed
Sep 2019	At least one fabricated jellyroll SAW LIB 20700 cell battery produced and suitable for future fast charging (a 6 C) protocols to >250 cycles.	Completed
Dec 2019	A report of the quantitative results demonstrating the jellyroll SAW LIB 20700 battery design, with recommendation for final design.	Completed
March 2020	Confirm performance of the final design, identify discrepancies, and report small-batch manufacturing and testing results.	Ongoing*
June 2020	Delivery of 18 jelly roll 2 Ah LIB and 2 circuit boards per the Q8 milestone specifications to the Department of Energy.	Ongoing*
*Behind due to complete lab and campus shutdown from mid-March 2020 to date due to COVID19.		

Approach

- We seek to enhance Li ion diffusion by inducing rapid electrolyte advection from acoustic streaming in the interelectrode gap, including the porous separator.
- We aim to enable fast charge lithium-ion batteries while maintaining their energy density. Our effort is in improving two performance aspects: (1) the SAW device and (2) the baseline cell

(1) Improving SAW device

- Design & performance optimization of the SAW device tailored to the battery
- Material characterization of cycled batteries to improved the SAW device design
- μPIV (particle image velocimetry) within transparent battery model
- Closed-form analysis model of acoustically driven fluid flow to produce design equations

(2) Improving baseline cell

- Electrode materials
- Electrolyte components
- Temperature effects
- Tuning charging modes (CC, CV)

Accomplishments

- Stable cycle performance to at least 2000 cycles for a SAW LIB cell charged in 15 mins and discharged at C/3, delivering 100 Wh/kg in the initial cycling and retaining 78% after 2000 cycles. Compare to identical no-SAW LIB cell: 55 Wh/kg and near-zero capacity after 50 cycles.

- We improved the energy density of our prototype SAW LIB cells from 110 Wh/kg to 160 Wh/kg in six months.

- Characterization of cycled LI batteries via SEM/EDX, XRD, and neutron diffraction analysis conclusively indicate electrode and electrolyte degradation is reduced with SAW

- Preliminary transparent battery flow experiments indicate distributed acoustic wave attenuation through battery causes acoustic streaming and inter-electrode flow

- SAW operating circuit is now a 5x5x0.25 cm structure, allows SAW operation off of primary charging circuit.

Responses to previous year’s reviewers’ comments

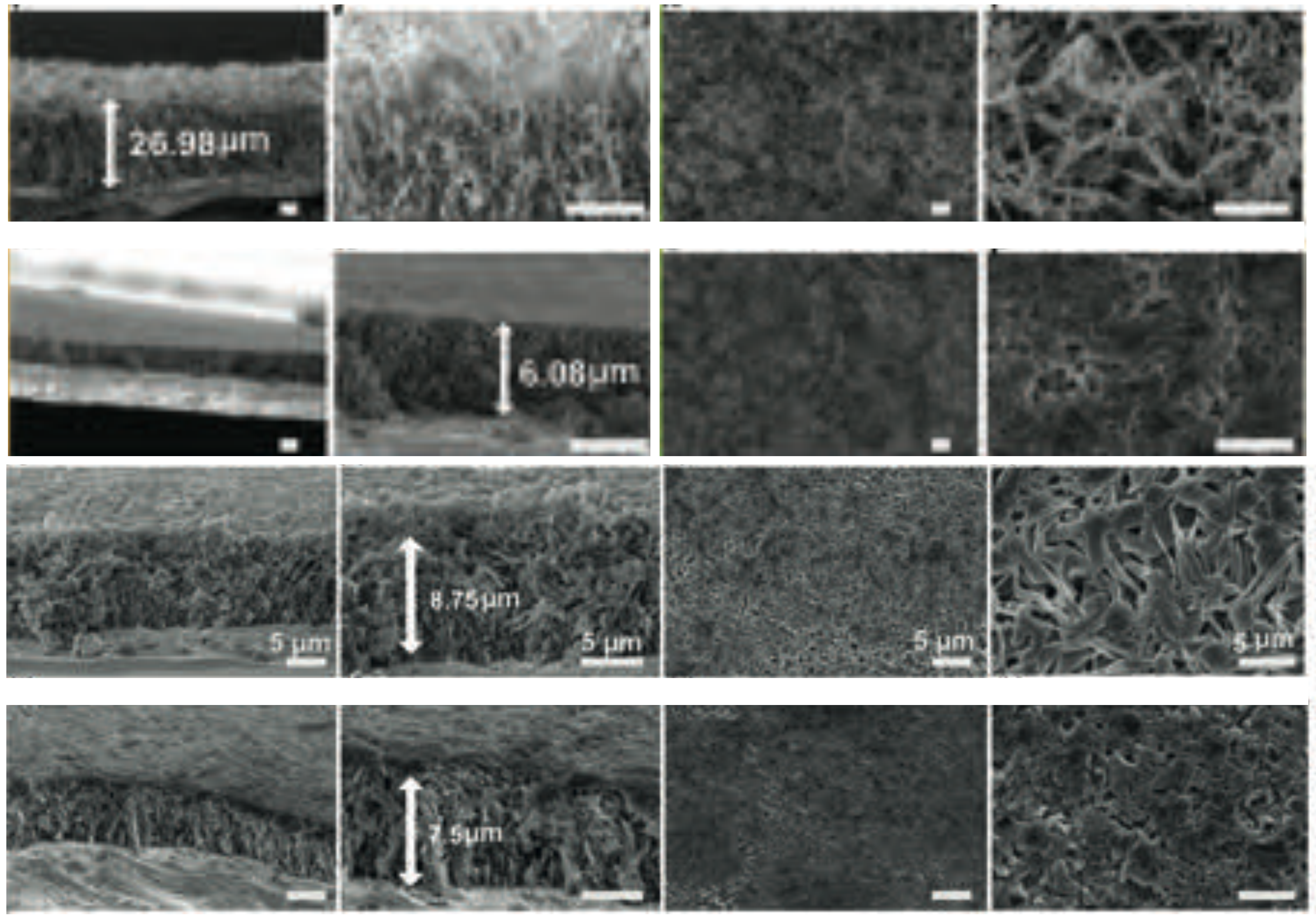
- Q1 (Approach to performing the work), Q4 (Proposed future research), and Q5 (Relevance):
  The 3 reviewers provided positive feedback on these three questions
- Q2 (Technical accomplishment):
  - The reviewer noted that 100% SAW on results in a large drop in Coulombic efficiency, for reasons not well understood.
  - Response: This likely refers to the different SAW power input which affects Li plating and consequently the Coulombic efficiency

Baseline cell:
SAW power: 0 mW

At sufficient power:
100 mW

At low power:
40 mW

At high power:
500 mW



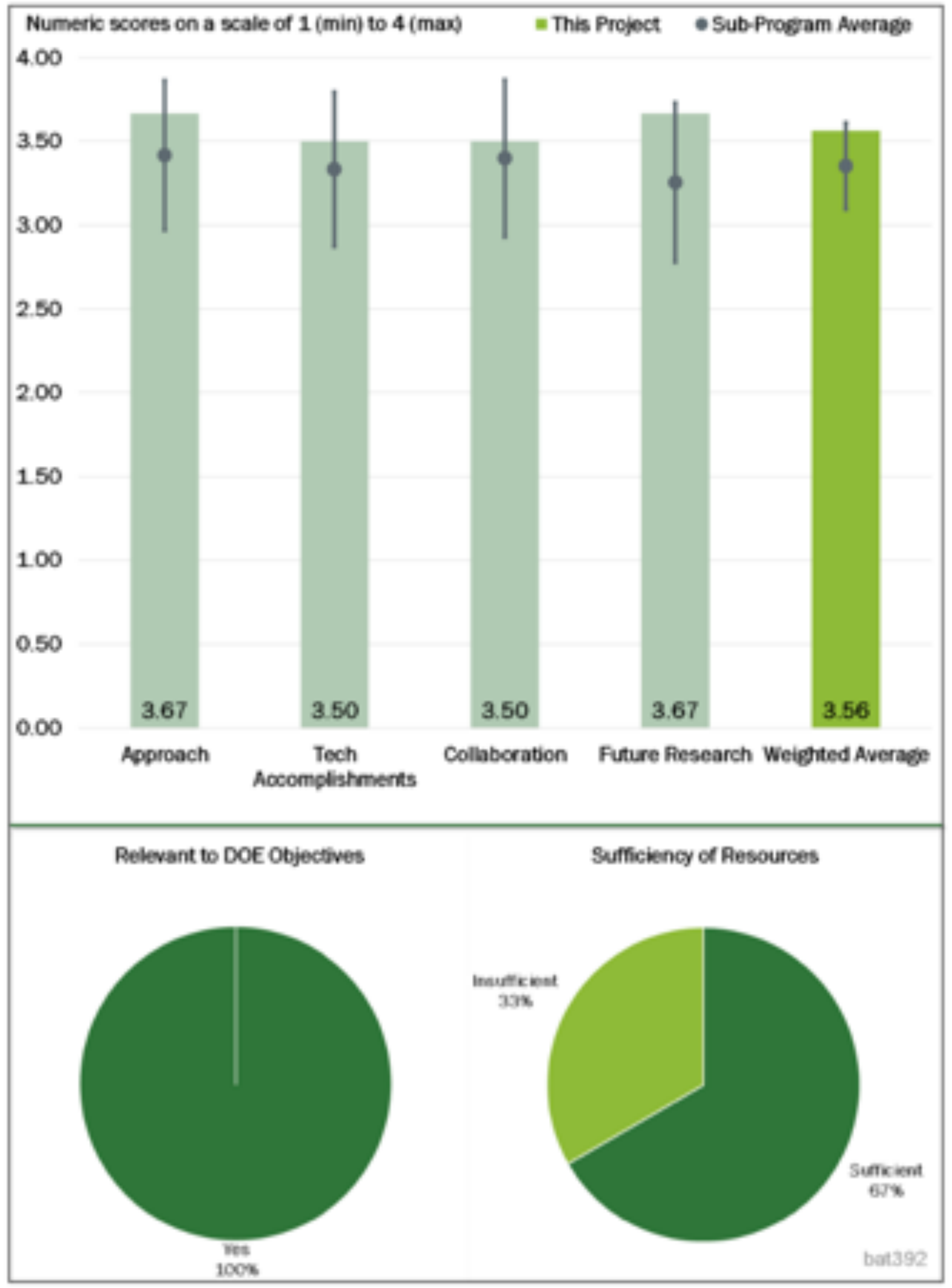


Figure 2-68 – Presentation Number: bat392 Presentation Title: Enabling Rapid Charging in Lithium-Ion Batteries via Integrated Acoustofluidics Principal Investigator: James Friend (University of California at San Diego)

Ref) https://www.energy.gov/sites/prod/files/2020/02/f71/Chapter_2_Batteries_R%26D_0.pdf

Responses to previous year's reviewers' comments

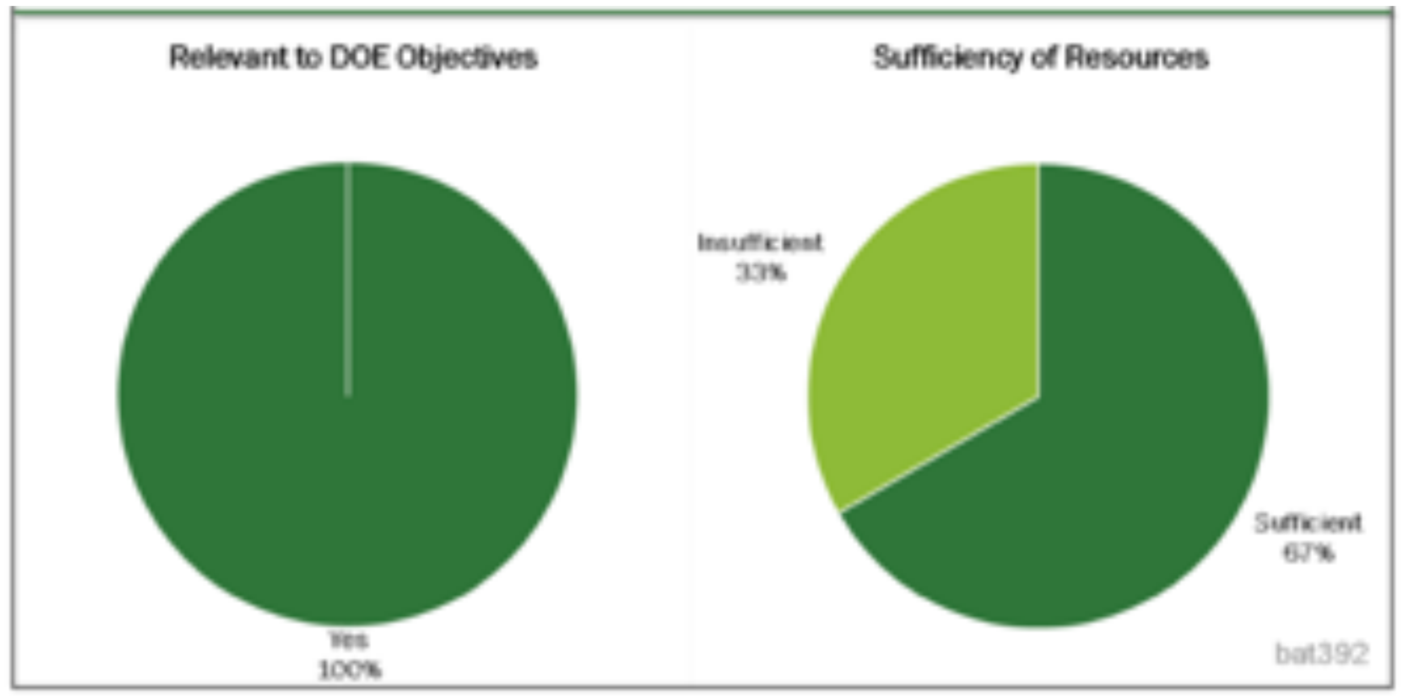
- Q2 (Technical accomplishment, continued):
  - The reviewer indicated that a mathematical model of macro-transport near the anode surface with and without acoustic wave agitation was also developed. A Peclet based correlation was identified for predicting when the geometry (height) of surface asperities at the anode surface will result in Li-metal plating. The reviewer said **the exact connection between the modeling work and experiments is not entirely clear**, and asked **how the model will be used to identify the best way to implement acoustic wave electrolyte agitation.**
  - *Response: At last year's presentation, the model was preliminary. Since then, we have*
    *- **constructed flow experiments with transparent battery structures** to precisely match the inter electrode electrolyte gap and the porous separator, and **in-situ neutron imaging** (ONRL) for the actual LIB,*
    *- **tested LIBs with purposely sub-optimal SAW operation** and found dendrite formation and dendrite suppression in the same battery in regions **predicted by the analysis,***
    *- **completed computational-based modeling** incorporating acoustic streaming, ion transport, and ion deposition that **matches the analysis**,*
    *- **designed new SAW LIBs with the analysis**; these LIBs are much improved.*

Ref) https://www.energy.gov/sites/prod/files/2020/02/f71/Chapter_2_Batteries_R%26D_0.pdf

Responses to previous year's reviewers' comments

- Q6 (Resources): The reviewer said that more resources will help to characterize the effect of this system over long-term operation, and to build it in large format cells.

- *Response: We are*
  - working with ORNL on neutron diffraction characterization to understand the in-situ effect of SAW-driven acoustic streaming on the LIB's components' morophology after long-term operation.
  - working with a manufacturer to provide high-performance 2Ah baseline cells; the same company is interested in integrating the SAW devices into these high performance cells.



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Collaboration and coordination

- UC San Diego's *Qualcomm Institute*: Charger circuit design and testing

- *Oak Ridge National Laboratory*: Neutron characterization on cycled Ah pouch cells.

- *LiFung Battery Manufacturer*: Producing commercial-grade large format pouch LIB cells.

Challenges and barriers

- Cell performance improves with SAW, but intrinsic battery characteristics still defines a trade-off between energy density and cycleability
- The baseline cell requires improvement to likewise improve the beneficial effect of SAW
  - Changing the electrolyte, charging modes (CC vs. CC+CV), and upper voltage limits produces **significant** improvements in the baseline LIB cell performance without SAW, and this must be combined with SAW in effort impacted by COVID-19
  - Increasing battery temperature enhances energy density but reduces cycleability
- With poor SAW design, electrode and separator morphology can vary across the battery depending on distance from SAW device: regions *farther away* show *faster degradation* (via optical imaging and in-situ neutron diffraction mapping): choice of SAW amplitude and frequency matters a **lot**

Ongoing and proposed future research

(1) Improving baseline LIB performance

- Tuning charging modes (CC, CV)
- Electrode materials: higher Ni content
- Electrolyte additives
- *Temperature effects*

(2) Improving LIB performance with SAW

- µPIV on transparent battery to improve math model used for design
- Ideal placement of SAW in large LIB?

(3) Avoid integration complexity: apply SAW from the *outside*

- Placing SAW device *in* battery a hassle
- Mount outside & retrofit *today's* batteries

(4) Apply SAW to low-cost, high energy LiS battery

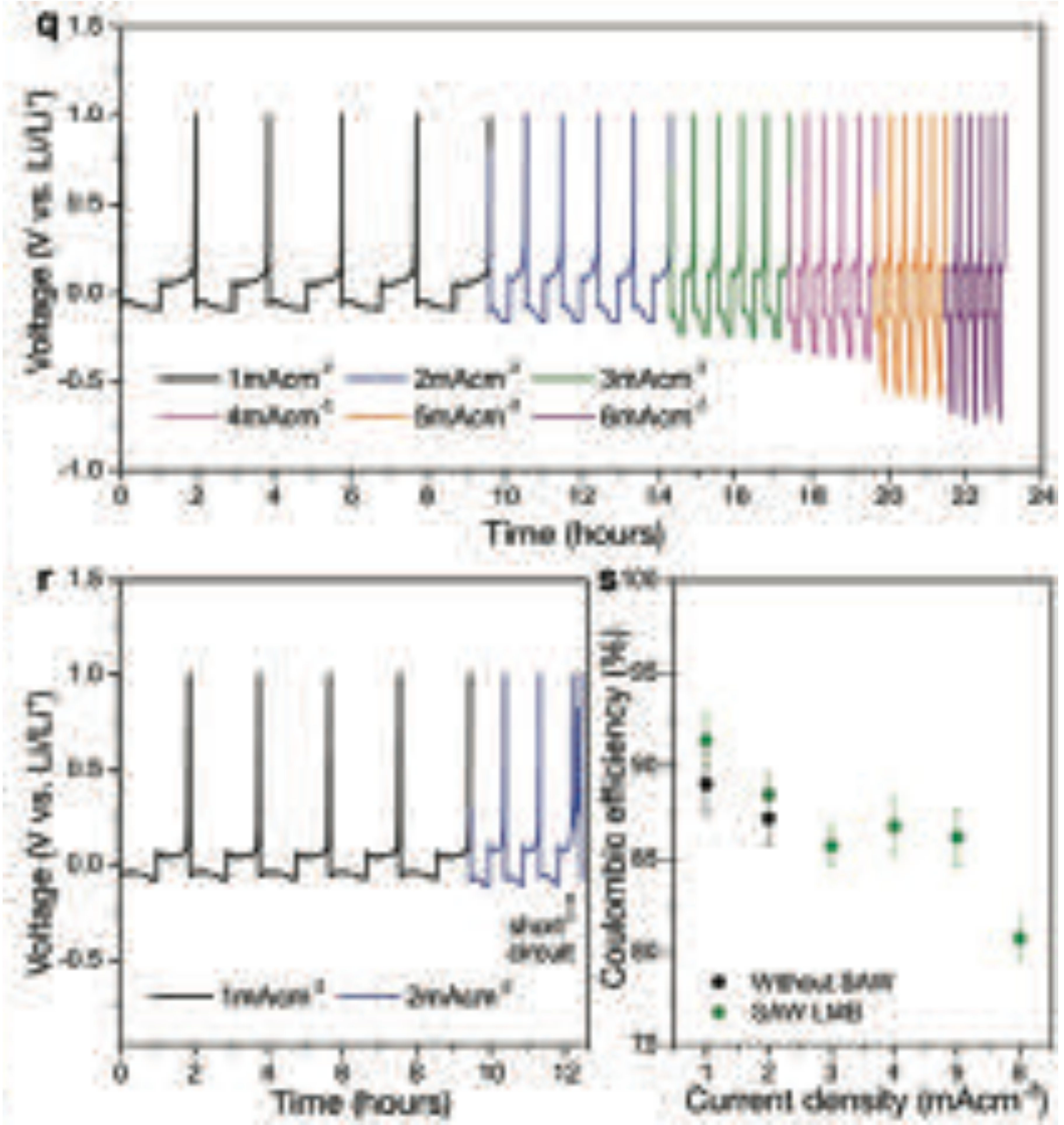
- The SAW-driven acoustic streaming approach is chemistry agnostic
- *Prove it beyond LIBs and LMBs*

Summary

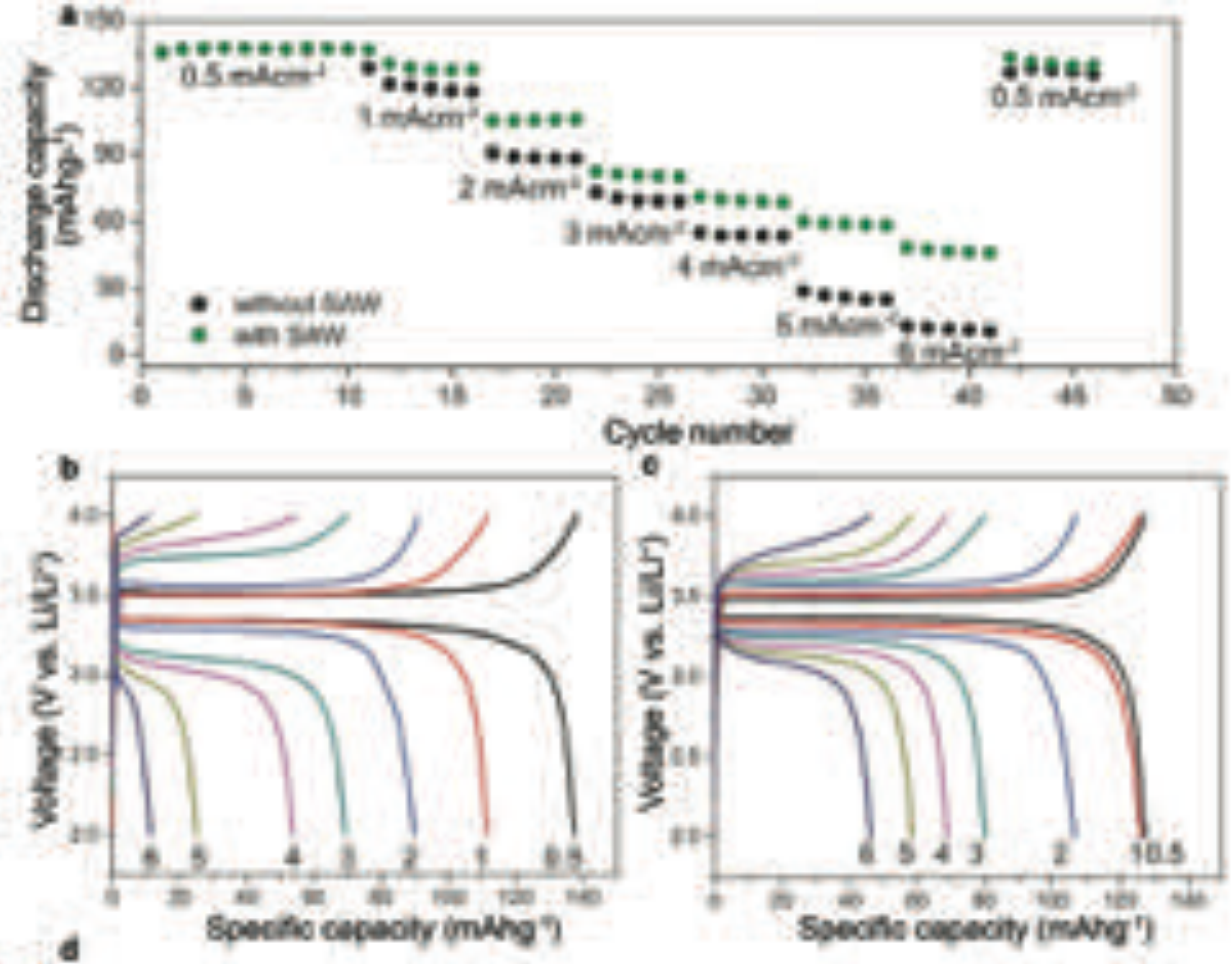
- **Technical highlights**
  - SAW *significantly* improves LIB cell performance under high charge rates
  - SAW *significantly* reduces LIB cell degradation
  - Miniaturization of the SAW driving circuit to a size consistent with use in batteries achieved
  - Significantly improved both power density and energy density of lithium batteries
- **Impact toward VTO objectives**
  - This work provides a potential way to greatly enhance rechargeable LIB performance during the charging cycle: (capacity) x (charge rate) x (lifetime) is significantly improved
  - Low cost (especially at scale), easy scale up, and appears to be commercially viable
  - Potentially retrofit technology

Cycling performance of a lithium metal battery

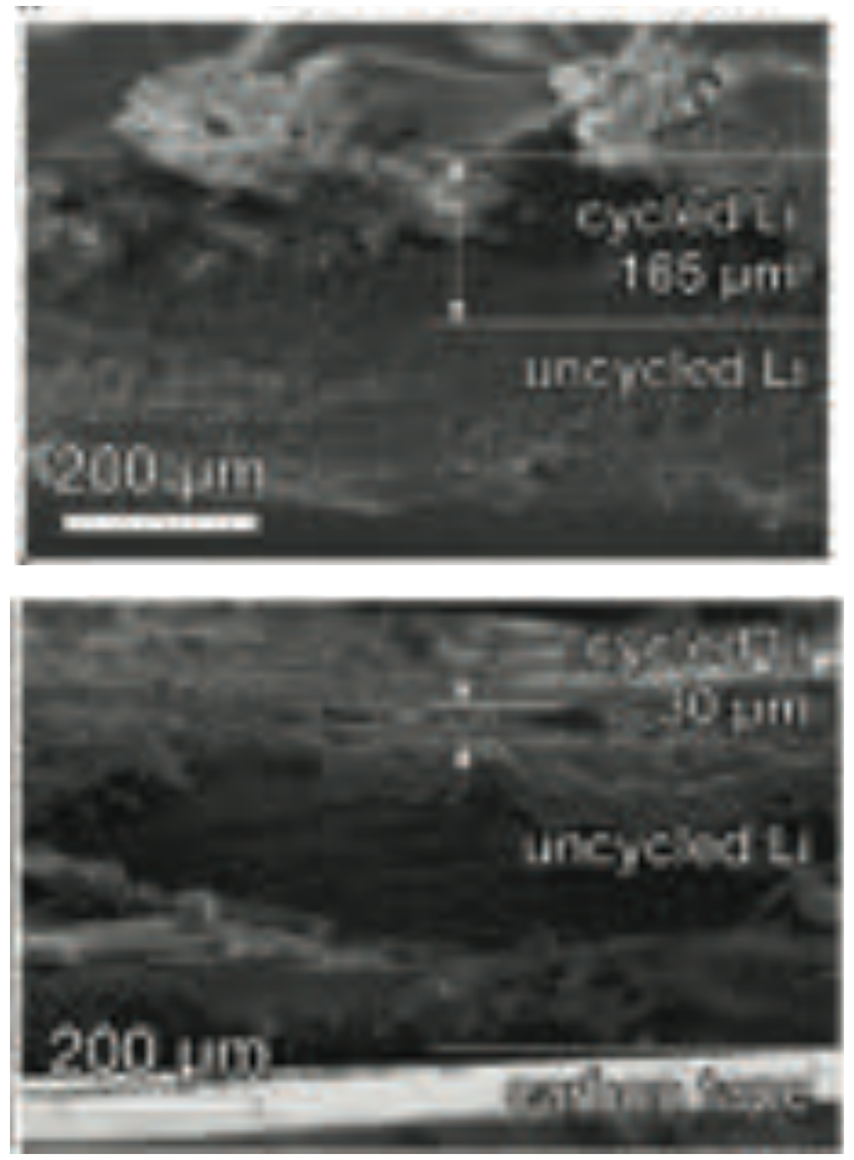
Technical backup



SAW Li||Cu cell shows stable cycle performance even at 6C rates, otherwise short circuited at 2C with EC/DEC electrolyte

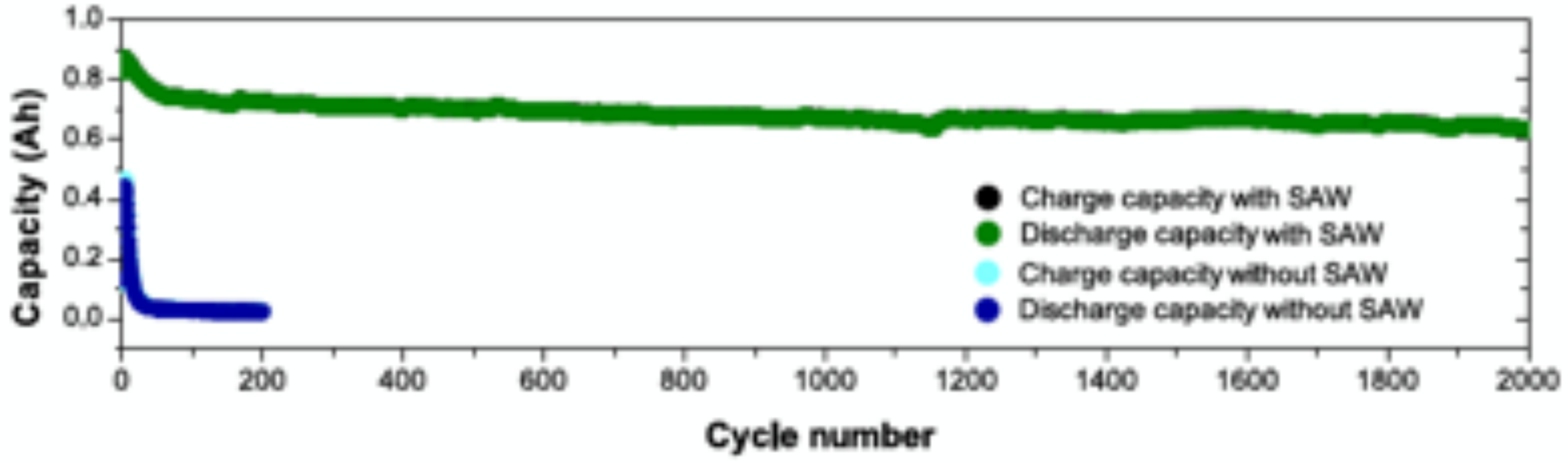


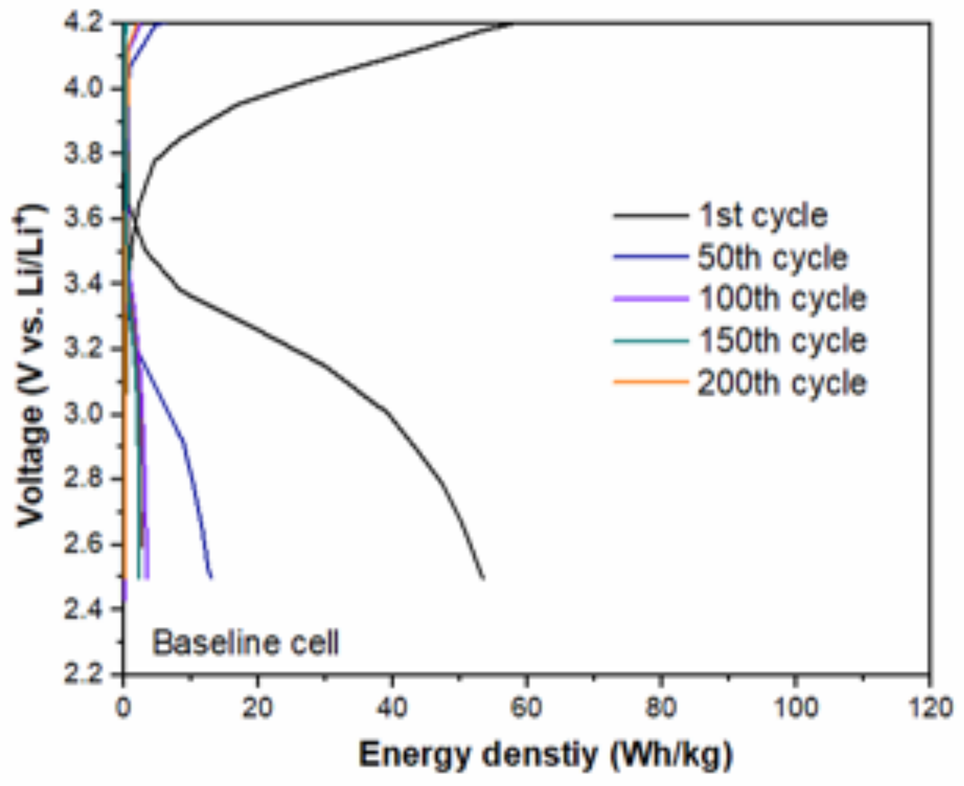
SAW Li||LFP cell shows better capacity retention when the charge rate increase from 0.5 to 6mAcm-2.

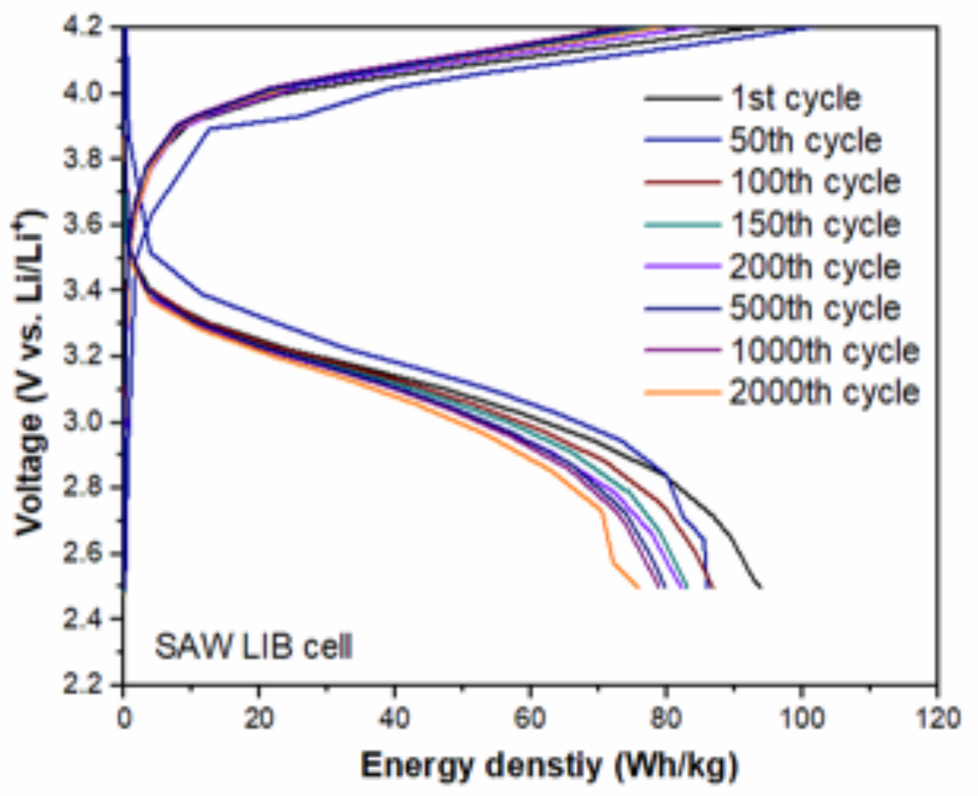


After 200 cycles, the Li consumption ratio is 5 times lesser of a SAW Li||LFP cell than a Li||LFP cell (8% vs. 40%)

Performance and characterization of 2Ah LIB



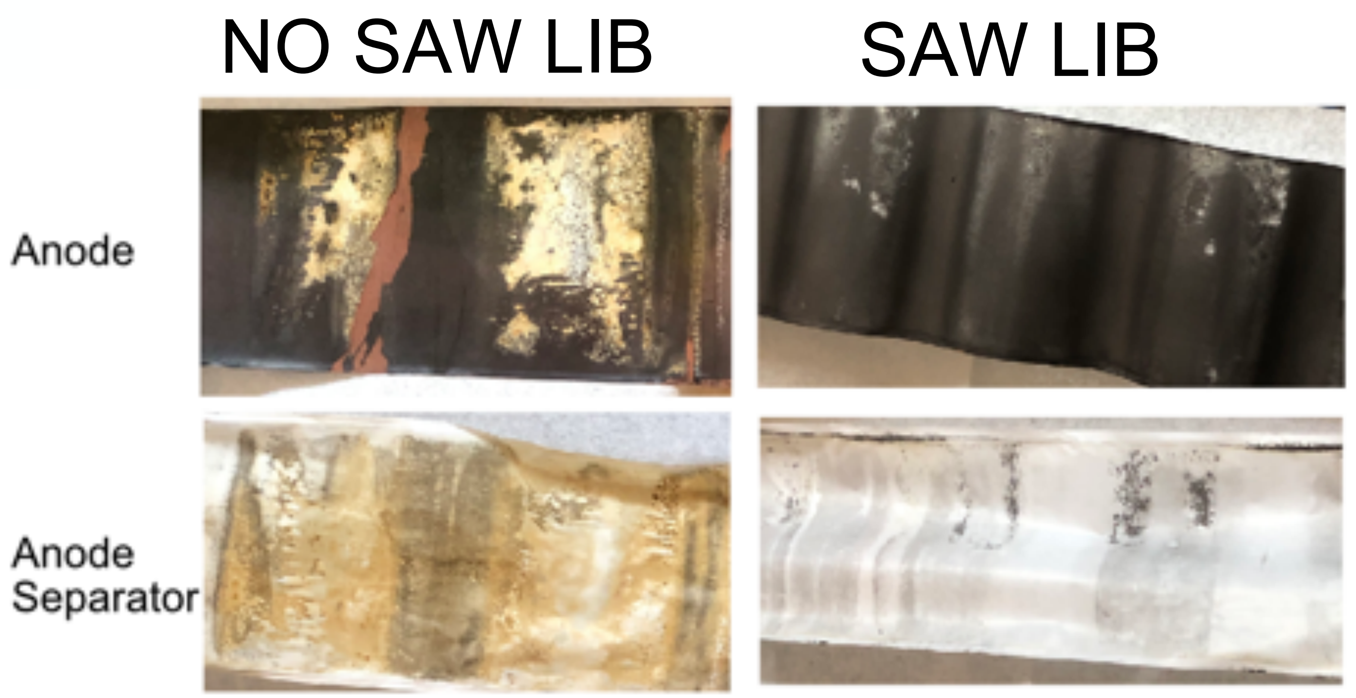




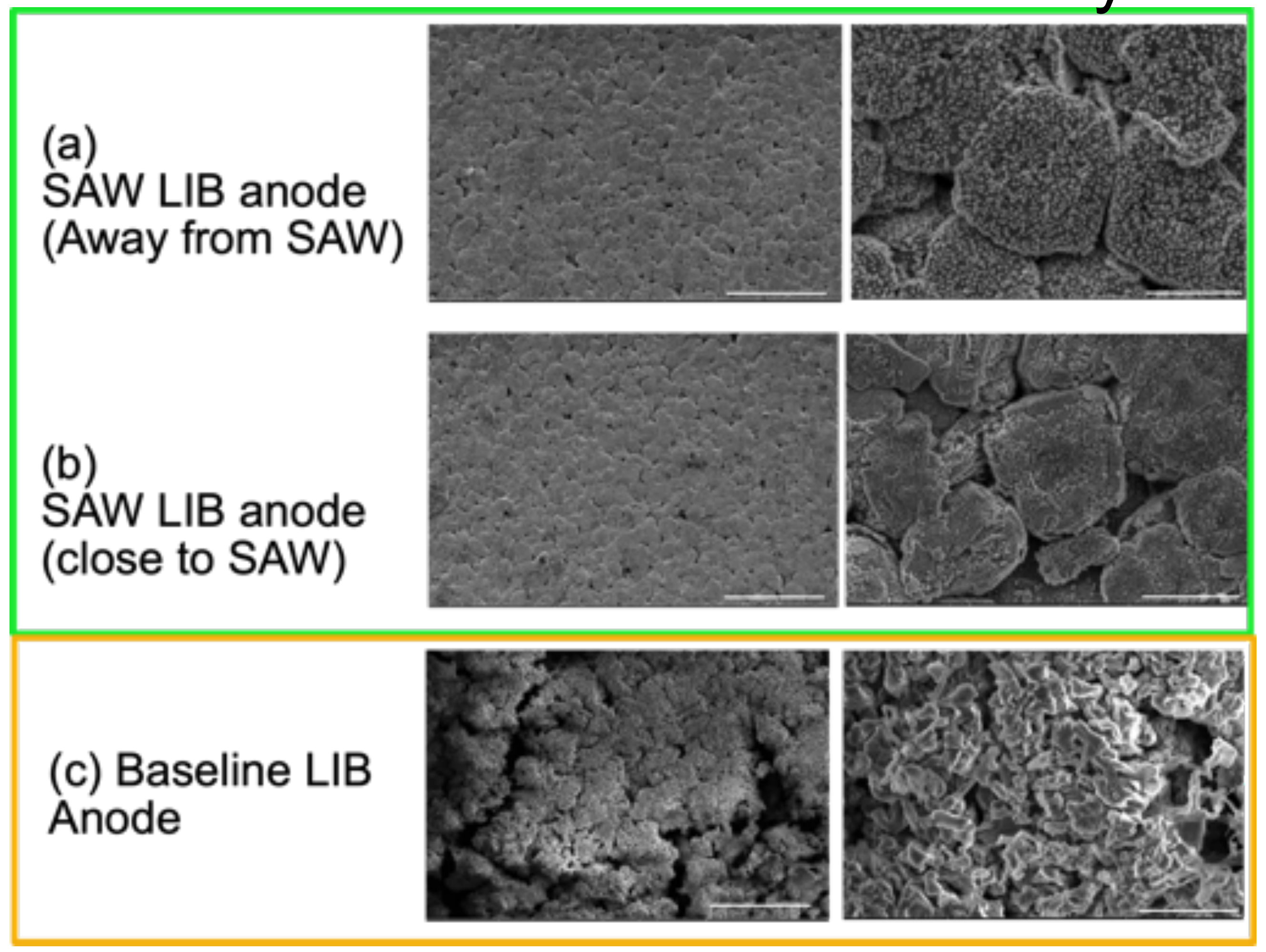
Cycle performance of an LIB with and without SAW using 15 mins 0-100% charge, C/3 discharge.

The SAW LIB shows superior cycling performance, with the initial capacity of 0.9Ah (~100Wh/kg) and capacity of 78% at 2000 cycles. Without SAW, an identical cell delivers only 0.5 Ah (~55Wh/kg) at the initial cycle and retained almost no capacity after 50 cycles.

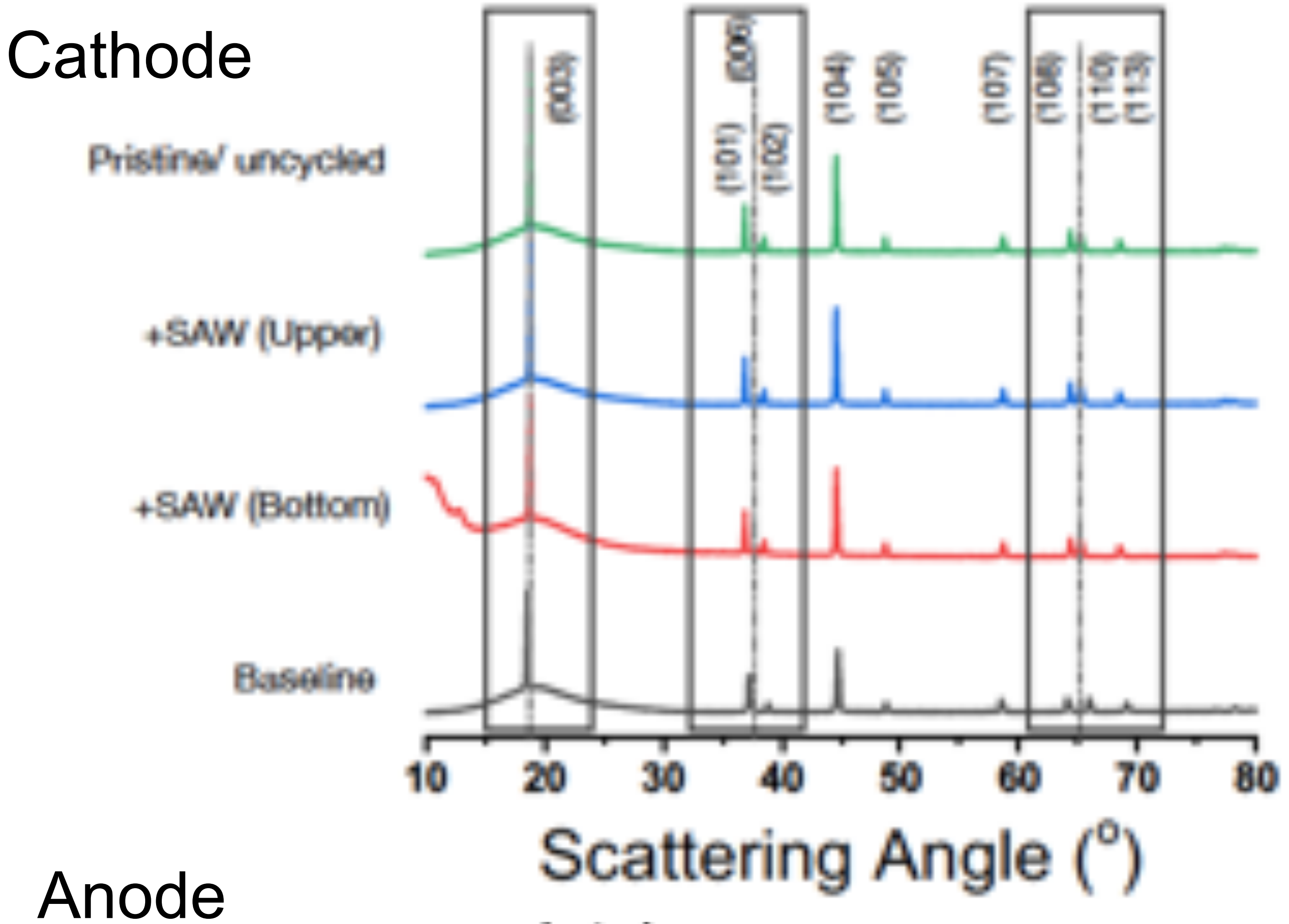
Technical backup

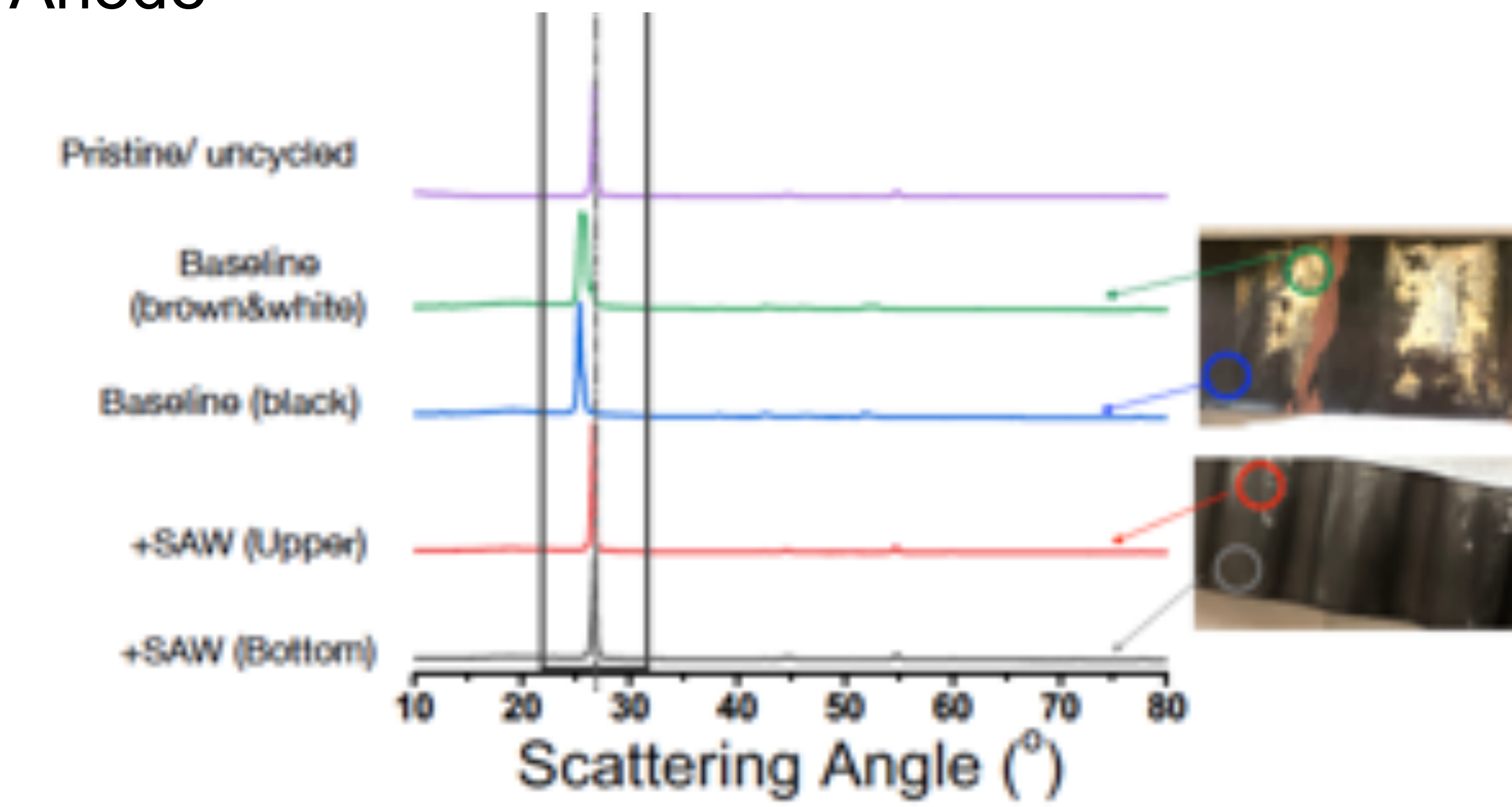


The baseline cell shows severe Li deposition after 200 cycles, while SAW LIB still remains clear after **2000** cycles.



(SEM) The electrode from cell w/o SAW indicates severe dendrite formation after 200 cycles; pristine graphite morphology remains after **2000** cycles with SAW

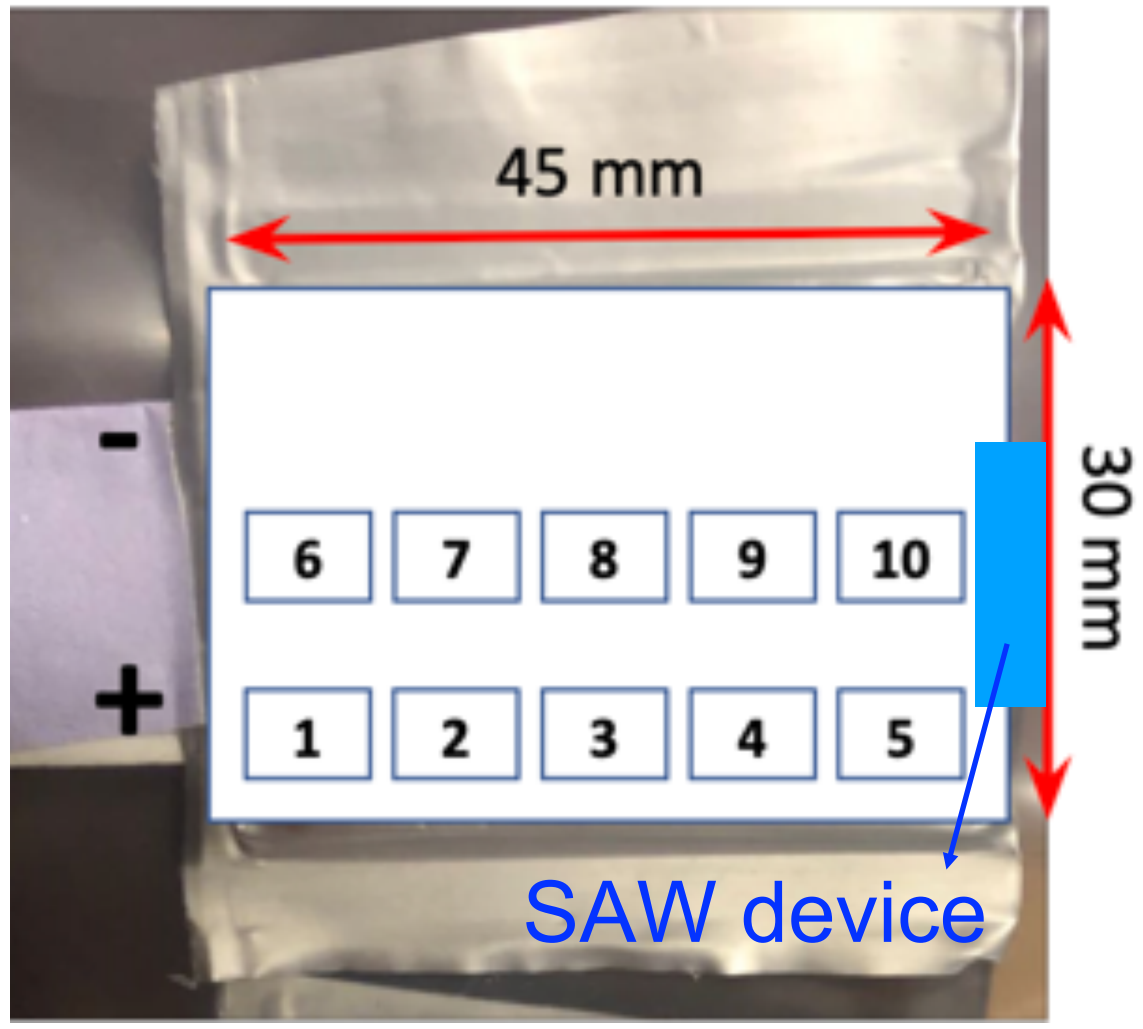




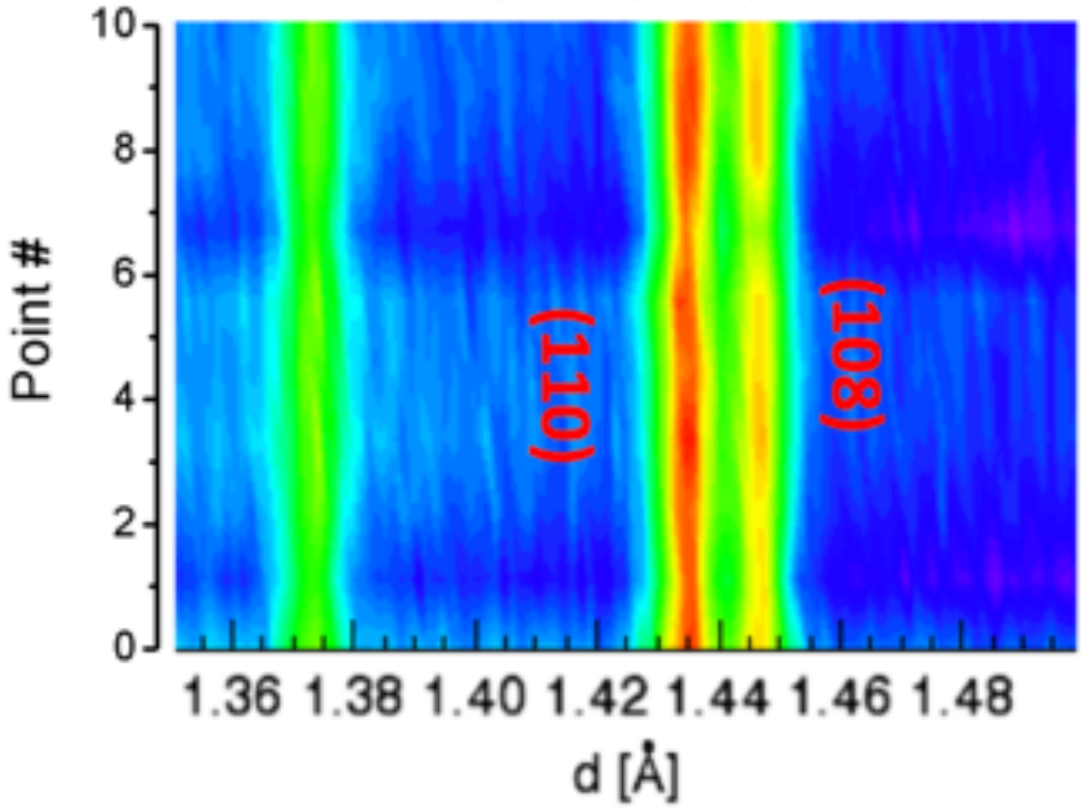
(XRD) Anode and cathode results indicate that **peak positions do not shift in cell with SAW**, but without SAW peaks significantly shift

Neutron diffraction characterization of 2Ah LIB

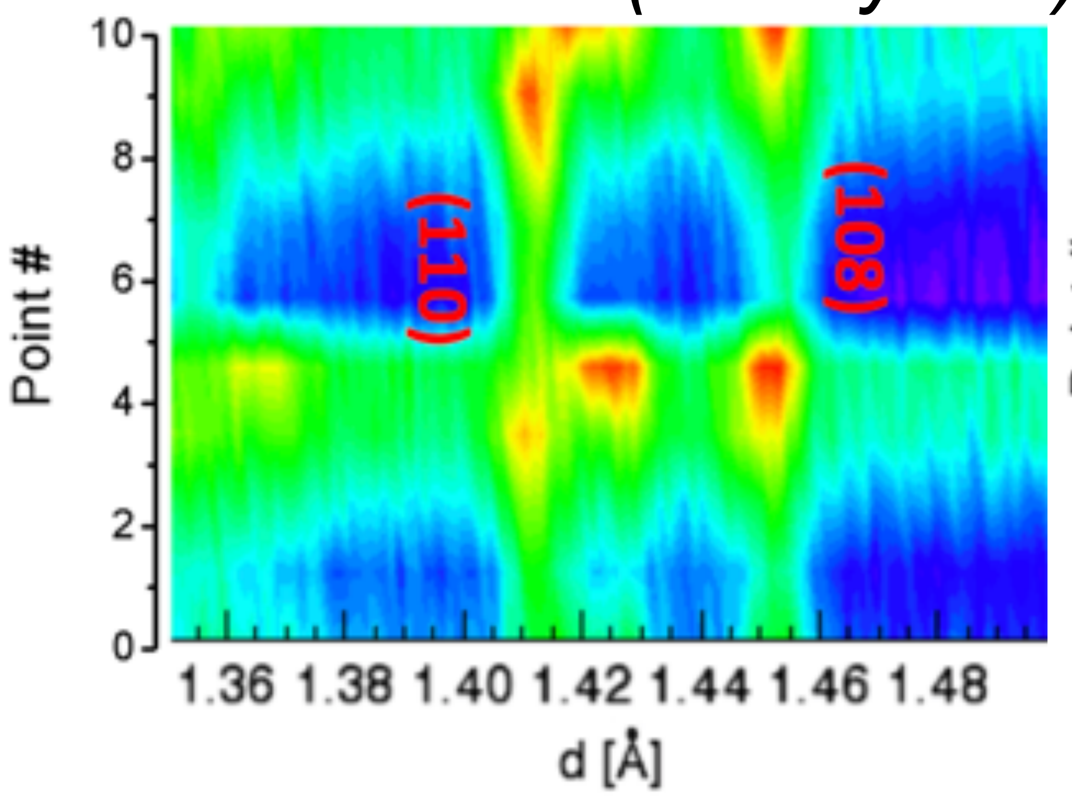
Technical backup



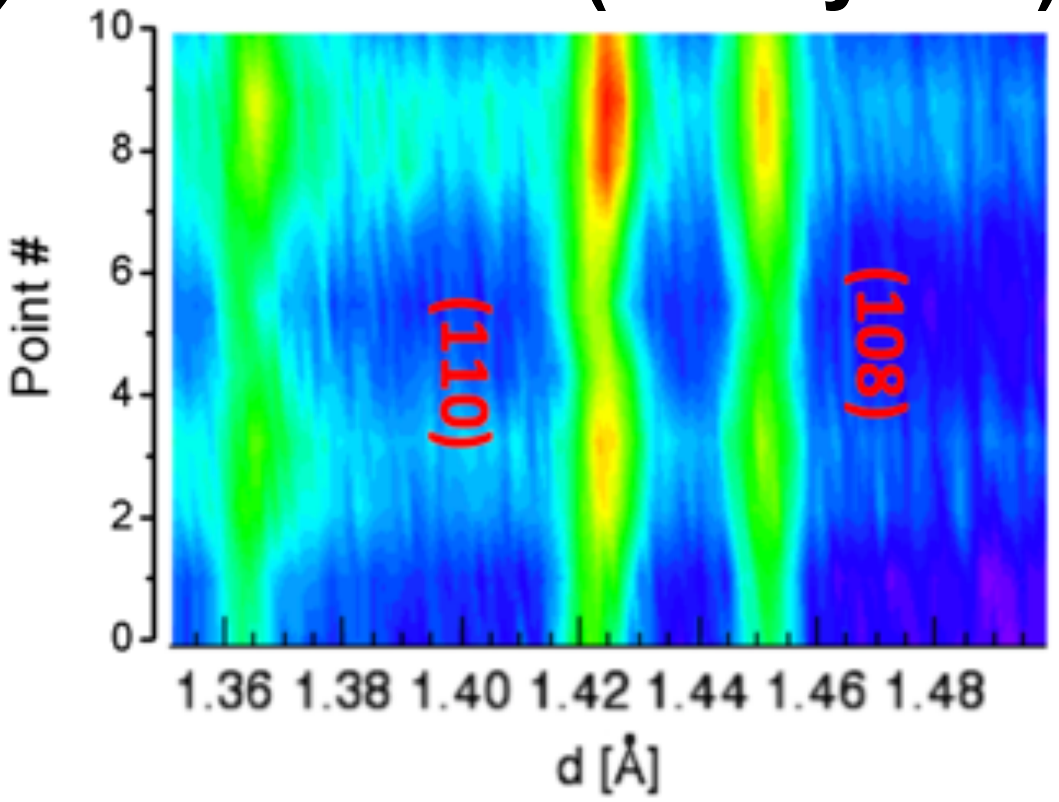
Pristine cell



NO SAW cell (250 cycles)

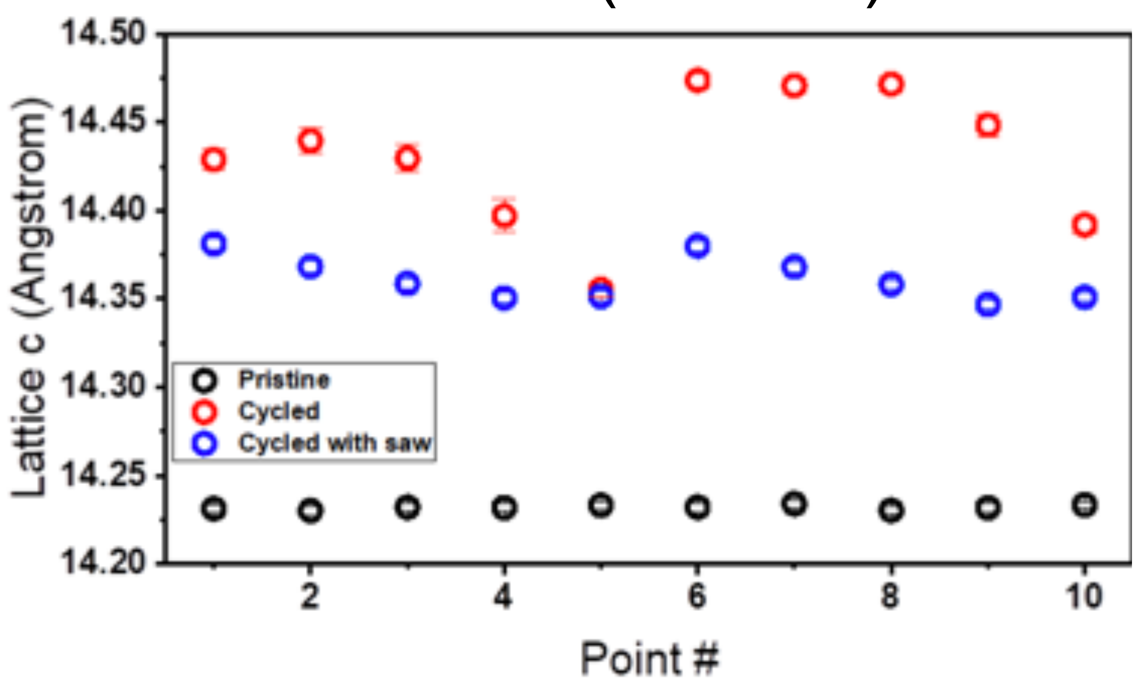


SAW cell (250 cycles)

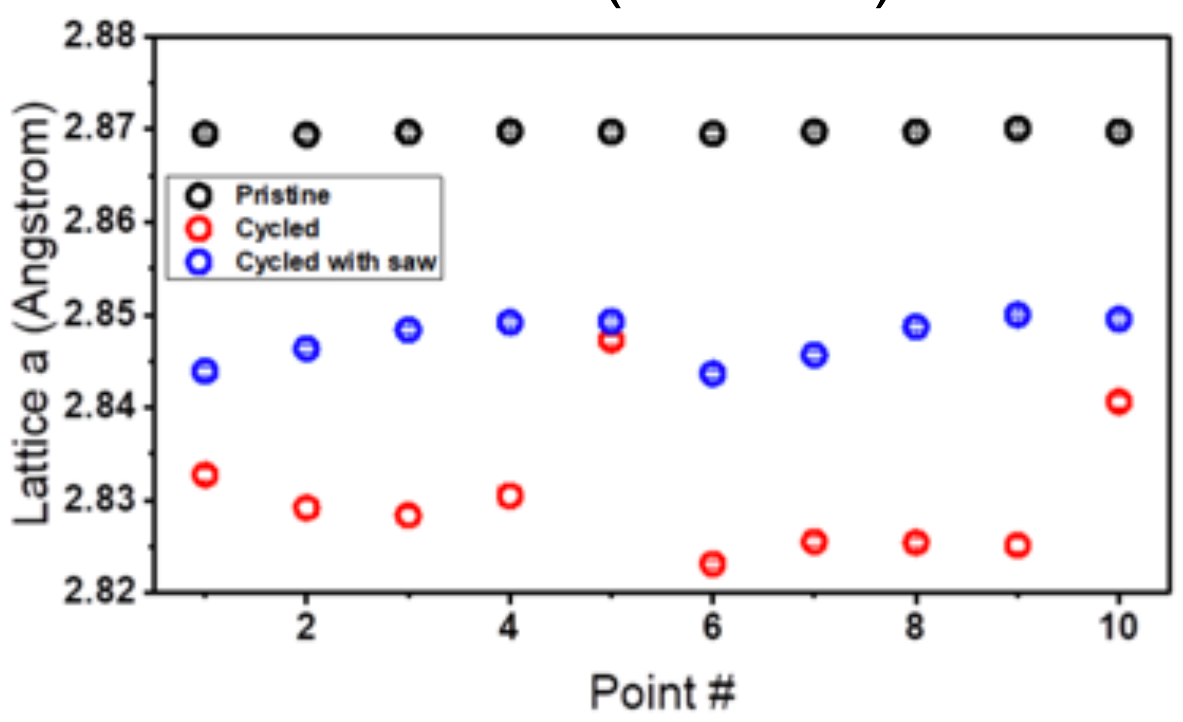


The pristine cell shows constant cathode peaks. *No SAW cell shows large variations in cathode peaks.* **The SAW cell shows fewer and weaker cathode peak variations.**

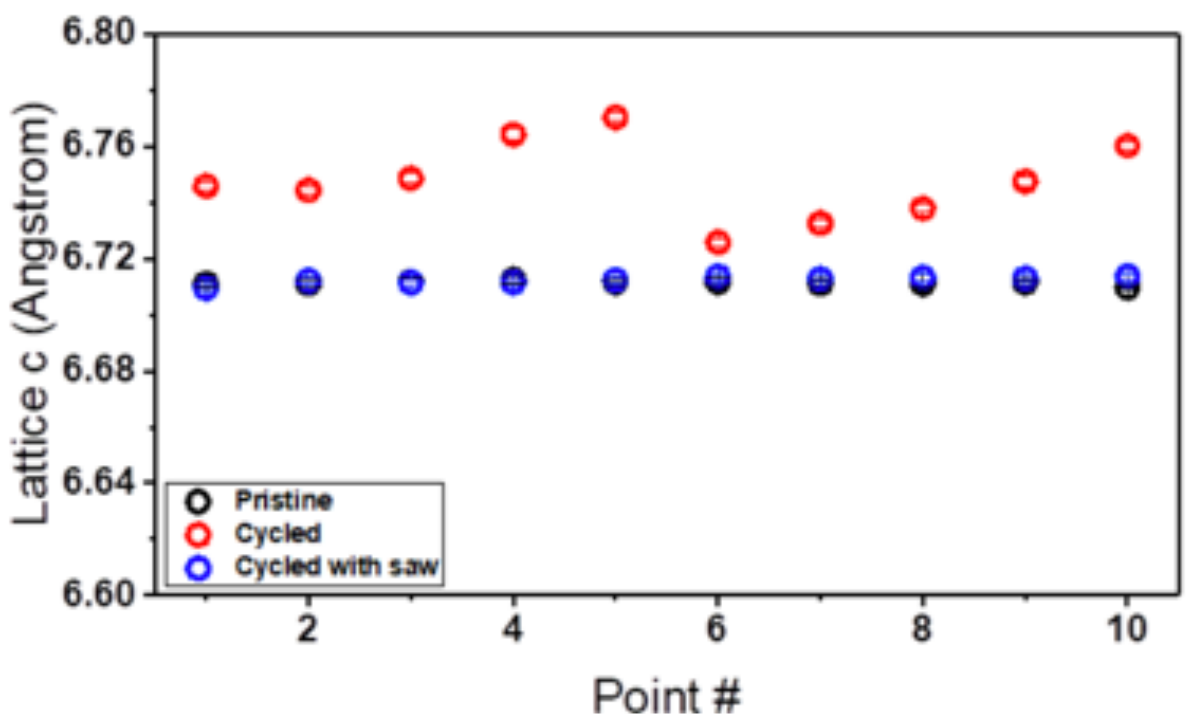
Cathode (c lattice)



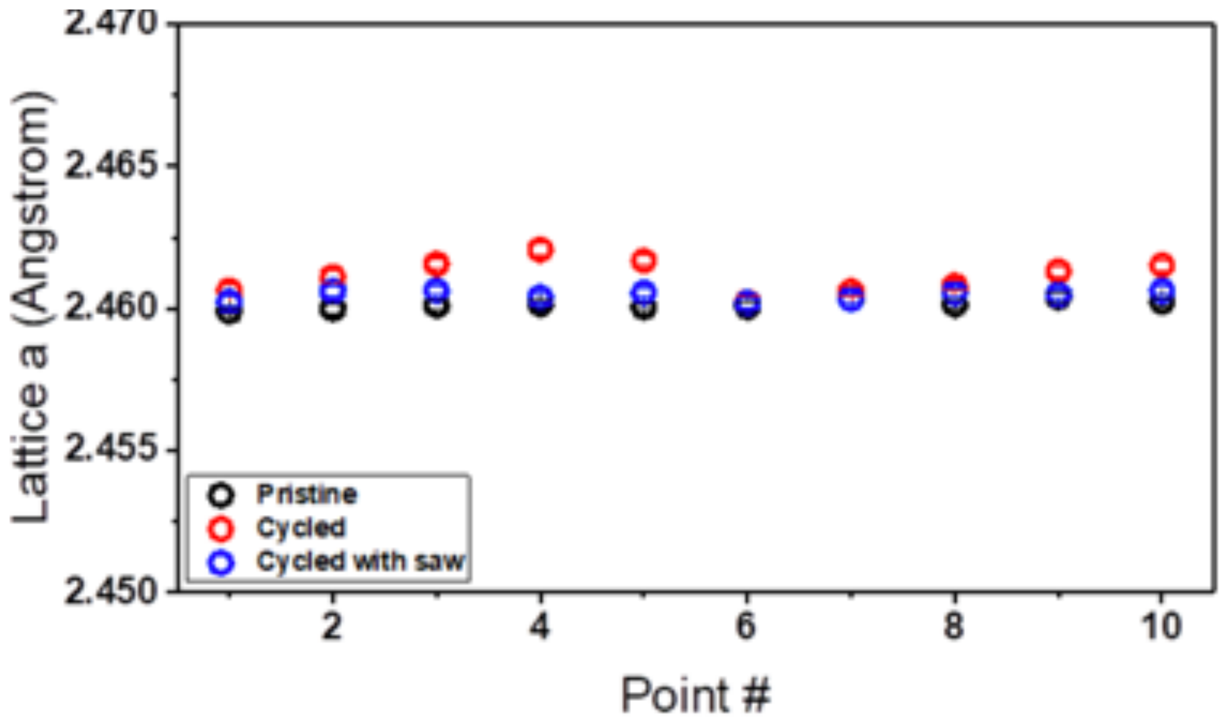
Cathode (a lattice)



Anode (c lattice)



Anode (a lattice)

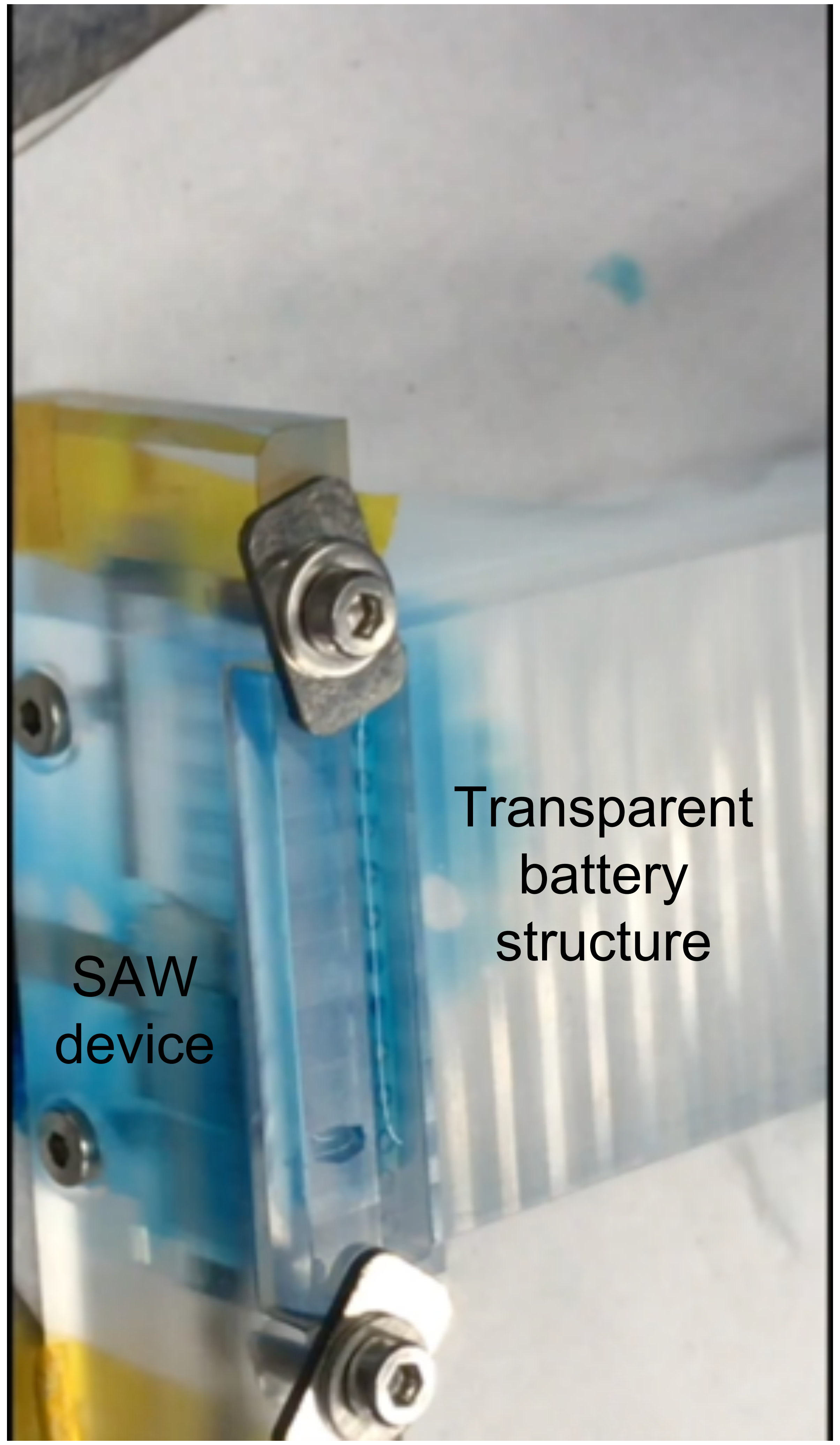


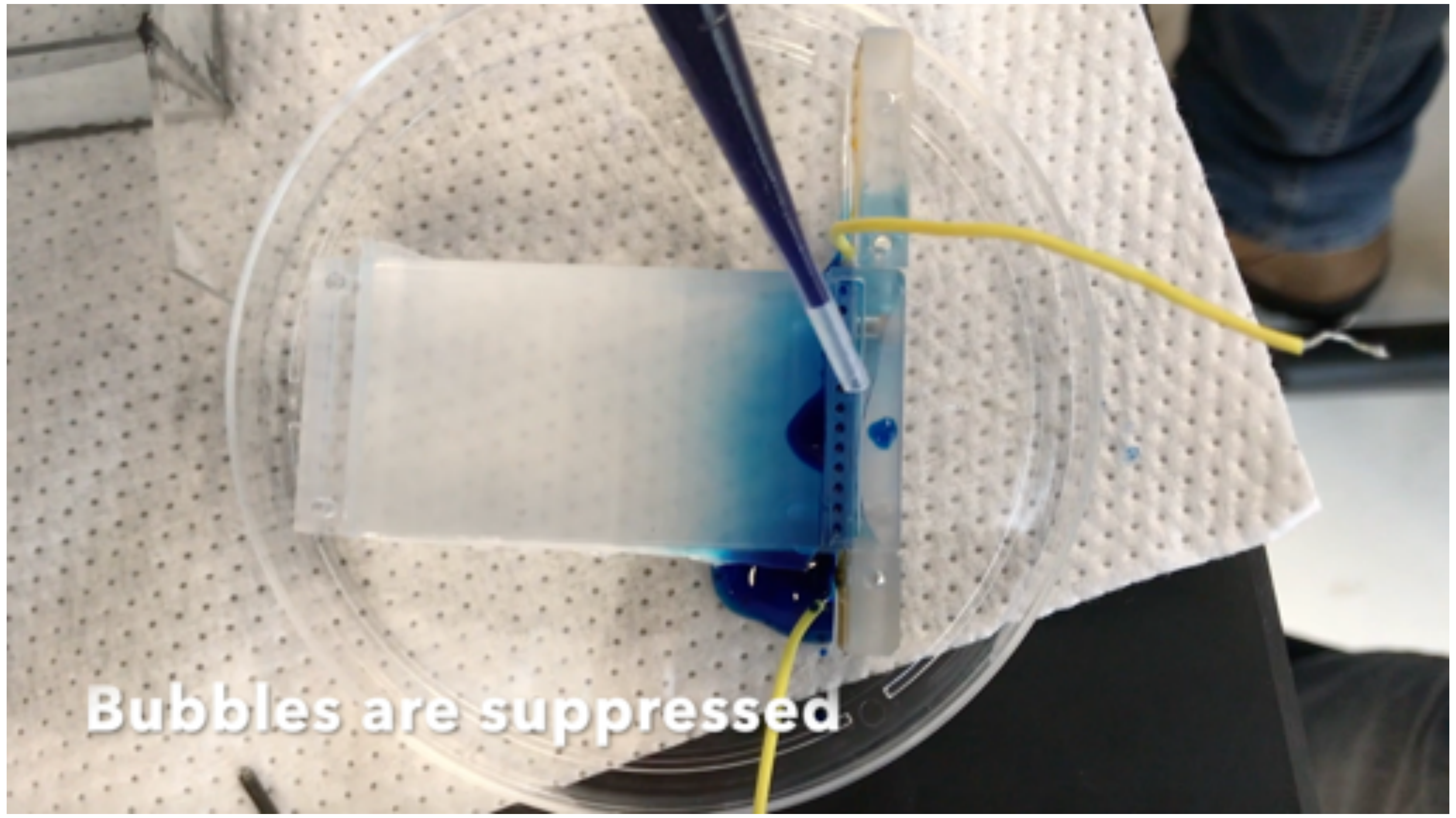
- Less Li loss with SAW
- Cathode degradation more uniform with SAW
- Cathode close to SAW degraded less

- Graphite anode degradation less obvious than cathode
- Graphite anode structure in SAW LIB similar to pristine cell

Transparent battery fluid flow results

Technical backup; impacted by COVID-19





Video 2: Bubbles are suppressed with new assembly method

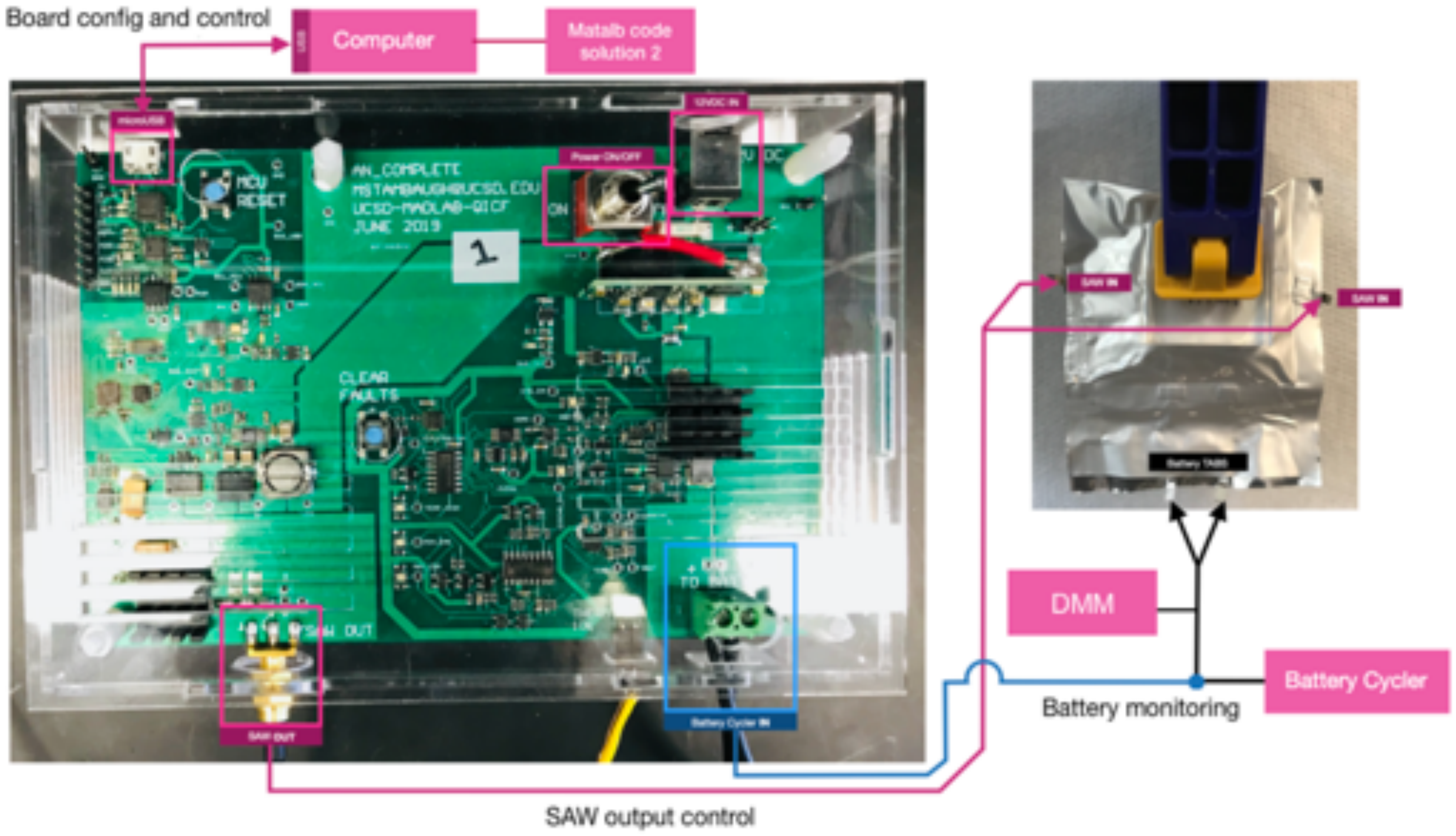
Video 1: Fluid transportation with SAW

- Battery structure: single inter-electrode layer with separator
- Prefilled with transparent deionized water
- Dyed water (dye molecule << pore size) introduced at SAW side of battery
- SAW drives acoustic streaming and transport of fluid: clear-colored fluid boundary transported away from SAW device in separator & inter electrode gap
- Undesired bubble formation during assembly

SAW driver circuit development

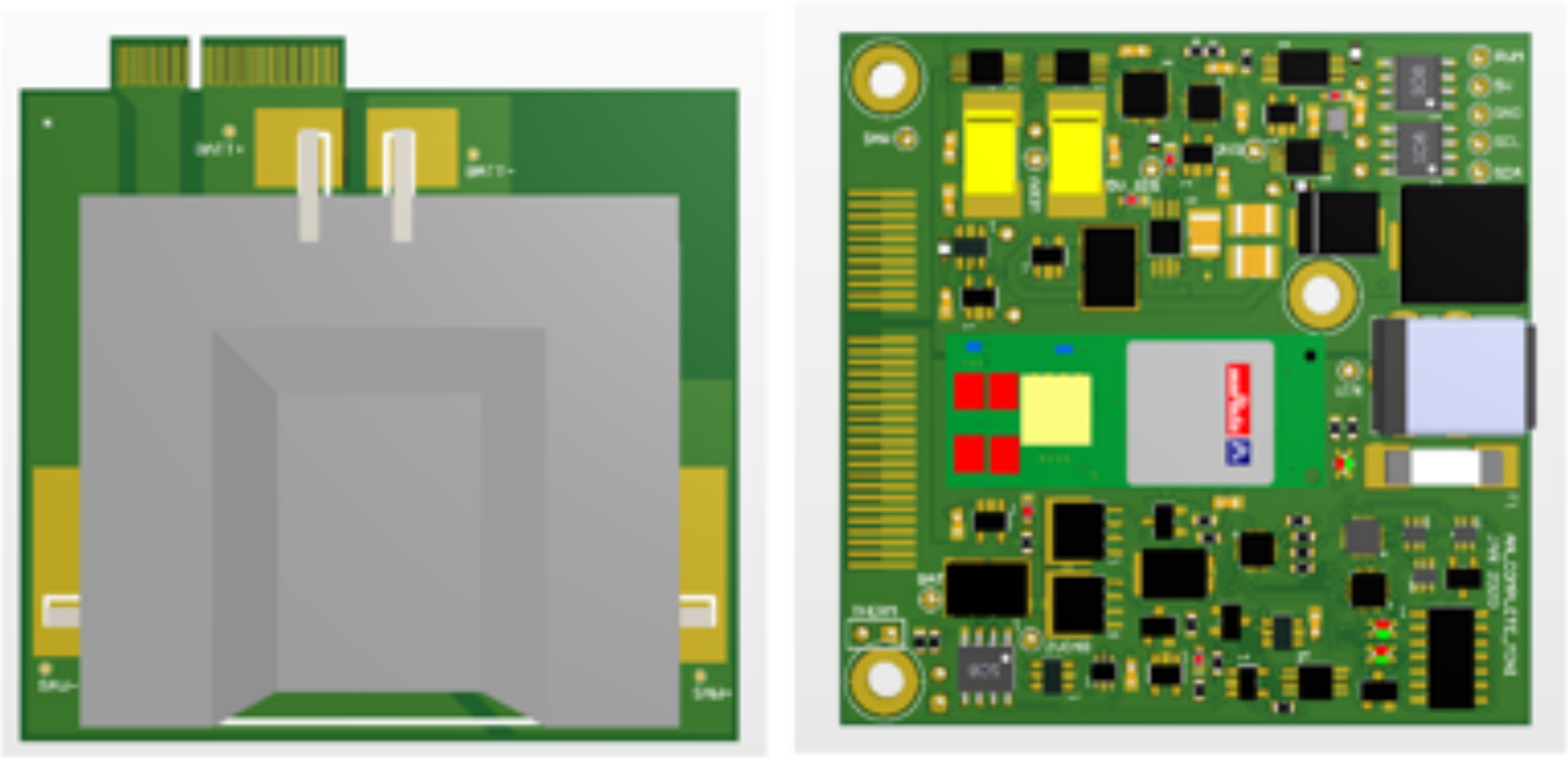
Technical backup; impacted by COVID-19

Version A (late 2019)



- Size 30W x 15L x 3T cm
- Includes battery charging function (to 30A) and SAW signal power control (40–200MHz, 2W output)

Version B (Q2 2020)



- Size 5W x 5L x 1T cm
- Includes battery charging function (to 30A), SAW signal power control (40–200MHz, 2W output), and direct mounting to battery

Publications and presentations

A. Publications:

- “Enabling rapidly rechargeable lithium metal batteries via surface acoustic wave driven electrolyte flow”, A. Huang, H. Liu, O. Manor, P. Liu, and J. Friend, Advanced Materials (2020)
- “Micro/nano acoustofludics: materials, phenomenon, design, devices, and applications”, W. Connacher, N. Zhang, A. Huang, J. Mei, S. Zhang, G. Tilvawala, J. Friend, Lab on a Chip (2018)
- “Fast charging lithium ion battery via surface acoustic wave driven electrolyte”, under preparation
- “Understanding acoustic streaming in porous media”, under preparation
- “Microcircuit design and fabrication for practical SAW acoustofluidics”, under preparation

B. Conference talks:

- Materials Research Society (MRS), Boston, MA (2019)
- Acoustical Society of America (ASA) annual meeting, San Diego, CA (2020)
- IEEE International Ultrasonics Symposium, annual meeting, San Diego, CA (2020)

C. Patents:

- Acoustic wave based dendrite prevention for rechargeable batteries, US 16/331,741
- Chemistry agnostic prevention of ion depletion and dendrite formation in a liquid electrolyte, provisional patent (filed)

Critical assumptions and issues

- LIB performance limitations due to cathode (532) and electrolyte choices. Partially solved, could be far better solution with provision of high-performance LIB from industry for testing in retrofit configuration (SAW device placed externally). Also could be aided by other chemistries, LiS and others.

- Ability to manufacture large numbers of batteries limited in a university environment. Partially solved with experience by graduate student and postdoc involved in project, could be better with industrial partner providing batteries for augmentation or introduction of SAW technology.

- COVID19 having outsized impact as remaining work is mainly experimental. Dealing with problem with analysis work during downtime.